JAN 18 2008
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PATENT & TRADEMARK OFFICE

Rev 06/04/04

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Victor L. Klimov et al.	Docket No.:	S-102,311
Serial No.:	10/715,733	Examiner:	Timothy J. Kugel
Filed :	November 17, 2003	Art Unit:	1712
For :	NANOCRYSTAL/SOL-GEL NANOCOMPOSITES		

Mail Stop Appeal Brief - Patents
Commissioner for Patents
PO Box 1450
Alexandria, VA 22313-1450

TRANSMITTAL OF APPEAL BRIEF

1. Transmitted herewith is the Appeal Brief in this application with respect to the Notice of Appeal filed on August 16, 2007.

2. Attached is a Fee Transmittal Form.

Respectfully submitted,

Date: January 16, 2008

Samuel L. Borkowsky
Signature of Agent

Reg. No. 42,346
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Samuel L. Borkowsky
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CERTIFICATE OF MAILING/TRANSMISSION (37 CFR 1.8(a))

I hereby certify that this correspondence is, on the date shown below, being:

MAILING

☒ deposited with the United States Postal Service on the date shown below with sufficient postage as first class mail in an envelope addressed to the: Commissioner for Patents, PO Box 1450, Alexandria, VA 22313-1450.

Date January 16, 2008

FACSIMILE

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Samuel L. Borkowsky
Signature

Samuel L. Borkowsky
(type or print name of person certifying)

JAN 18 2008

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Rev. 02/02/06

FEE TRANSMITTAL
For FY 2006

Patent fees are subject to annual revision

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT: $255.00

Complete if Known	
Application Number:	10/715,733
Filing Date:	November 17, 2003
First Named Inventor:	Victor L. Klimov
Examiner Name:	Timothy J. Kugel
Group/Art Unit:	1712
Attorney Docket No.:	S-102,311

METHOD OF PAYMENT (check all that apply)

1. ☒ The commissioner is hereby authorized to charge indicated fees and credit any over payments to:
   Deposit Account Number: **12-2150**
   Deposit Account Name: **Los Alamos National Laboratory**
   ☒ Charge Any Additional Fee Required Under 37 C.F.R. 1.16 and 1.17

FEE CALCULATION

1. COMBINED FILING FEE

Large Entity Fee		Small Entity Fee		Fee Description	Fee Paid
1001	$300	2001	$150	Basic Filing fee	$0.00
1004	$300	2004	$150	Reissue Filing fee	$
1111	$500	2111	$250	Search Fee	$0.00
1311	$200	2311	$100	Examination Fee	$0.00
1005	$200	2005	$100	Provisional Filing Fee	
1085	$250	2085	$125	Provisional Size Fee	

(for each additional 50 sheets that exceeds 100 sheets)

SUBTOTAL (1) $0.00

2. EXTRA CLAIM FEES/APPLICATION SIZE FEE

		Extra Claims		Fee from Below		Fee Paid
Total Claims	–20** =		X		=	$0.00
Independent Claims	–3 ** =		X		=	$0.00
Multiple Dependent			X 180		=	$0.00

*** or number previously paid, if greater; For Reissues, see below*

Large Entity Fee		Small Entity Fee		Fee Description
1202	$50	2202	$25	Claims in excess of 20
1201	$200	2201	$100	Independent claims in excess of 3
1203	$360	2203	$180	Multiple dependent claim, if not paid.
1204	$200	2204	$100	Reissue independent claims in excess of 3 over original patent
1205	$50	2205	$25	Reissue claims in excess of 20 over original patent

Total Claims Fee $_______

APPLICATION SIZE FEE

1081 $250 2081 $125.00 For each additional 50 sheets that exceed 100 sheets, including specification and drawings

SUBTOTAL (2) $ 0.00
(Include total of Claims Fees and Size Fee here)

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Fee ($)	Small Entity Fee Code	Fee ($)	Fee Description	Fee Paid
1051	$130	2051	$65	Surcharge – late filing fee or oath	
1052	$50	2052	$25	Surcharge – late provisional filing fee or cover sheet	
1812	$2520	1812	$2520	For filing a request for reexamination	
1251	$120	2251	$60	Extension for reply within first month	
1252	$450	2252	$225	Extension for reply within second month	
1253	$1020	2253	$510	**Extension for reply within third month**	**$510.00**
1254	$1590	2254	$795	Extension for reply within fourth month	
1255	$2160	2255	$1080	Extension for reply within fifth month	
1401	$500	2401	$250	Notice of Appeal	
1402	$500	2402	$250	**Filing a brief in support of an appeal**	**$255.00**
1403	$1000	2403	$500	Request for oral hearing	
1452	$500	2452	$250	Petition to revive – unavoidable	
1814	$110	2814	$55	Terminal Disclaimer	
1453	$1500	2453	$750	Petition to revive – unintentional	
1460	$130	1460	$130	Petitions to the Director	
1806	$180	1806	$180	Submission of Information Disclosure Statement	
1809	$790	2809	$395	Filing a submission after final rejection (37 CFR 1.129 (a))	
1810	$790	2810	$395	For each additional invention to be examined (37 CFR 1.129(b))	
1811	$100	1811	$100	Certificate of Correction	
1504	$300	1504	$300	Publication fee for early, voluntary, or normal publication/Republication fee	
1801	$790	2801	$395	Request for Continued Examination (RCE)	

Other fee (specify) ____________________

SUBTOTAL (3) $765.00

Reduced by Basic Filing Fee Paid

SUBTOTAL FROM 1	**$ 0.00**
SUBTOTAL FROM 2	**$ 0.00**
SUBTOTAL FROM 3	**$ 765.00**
TOTAL AMOUNT OF PAYMENT (Enter total amount at top of page)	**$765.00**

SUBMITTED BY			Complete (if applicable)	
Printed Name:	Samuel L. Borkowsky		Reg. No.	42,346
Signature:	Samuel L. Borkowsky	Date: January 16, 2008	Telephone	(505) 665-3111

01/30/04

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Appellants:	Victor L. Klimov et al.	Docket No.:	S-102,311
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APPEAL BRIEF

TABLE OF CONTENTS

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Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

REAL PARTY IN INTEREST

Los Alamos National Security, LLC is the assignee of all right, title, and interest in and to U.S. Patent Application Serial No. 10/715,733 from the Government of the United States, United States Department of Energy.

RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences.

STATUS OF CLAIMS

Claims 1-27 are pending in the application. Pending claims 1-12 and 17-27 have been finally rejected by an Office Action dated March 16, 2007. Claims 13-16 have been withdrawn from consideration. The rejection of claims 1-12 and 17-27 is appealed. No claims have been allowed.

STATUS OF AMENDMENTS

No amendments have been filed subsequent to the final rejection dated March 16, 2007.

SUMMARY OF CLAIMED SUBJECT MATTER

The claimed subject matter relates to a process of preparing a solid composite that includes colloidal nanocrystals dispersed within a sol-gel host matrix, and also to the reaction product of (i) colloidal nanocrystals complexed with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups and (ii) a sol-gel precursor material. The claim limitations and locations in the patent application for their support are summarized in the table below.

Claim Limitation	Support Location
1. A process of preparing a solid composite including colloidal nanocrystals dispersed within a sol-gel host matrix, the process comprising:	Page 3 lines 25-27; page 14 line 20 through page 17 line 7.
admixing colloidal nanocrystals with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups within a solvent to form an alcoholic-soluble colloidal nanocrystal-polymer complex;	Page 4 line 5 through page 5 line 16; page 6 lines 11-18; page 6 lines 24 through page 12 line 2; page 13 line 8-16; page 14 lines 20-26; page 15 lines 18-27; page 16 lines 12-19; page 16 line 26 through page 17 line 1.
admixing the alcohol-soluble colloidal nanocrystal-polymer complex and a sol-gel precursor material; and,	Page 11 line 22 through page 13 line 3; page 15 lines 1-4; page 15 line 27 though page 16 line 2; page 16 lines 19-22; page 17 lines 1-7.
forming said solid composite from said admixture.	Page 15 lines 1-4; page 16 lines 1-2; page 16 lines 19-22; page 17 lines 1-7.
2. The process of claim 1 wherein said colloidal nanocrystals have a volume loading of up to about 30 percent by volume within said solid composite.	Page 12 line 24 through page 13 line 1.
3. The process of claim 1 wherein said hydrophilic groups are selected from the group consisting of –COOH, -OH, -SO_3H, -NH_2, and –PO_3H_2.	Page 13 line 8-11.
4. The process of claim 1 wherein said sol-gel precursor material is selected from the group consisting of metal alkoxide compounds, metal halide compounds, and metal hydroxide compounds where the metal is selected from the group consisting of silicon, titanium, zirconium, aluminum, vanadium, iron, tin, tantalum, cerium, and chromium.	Page 12 lines 9-15.

5. The process of claim 1 wherein said colloidal nanocrystals are selected from the group consisting of M_1X_1, $M_1M_2X_1$, $M_1M_2M_3X_1$, $M_1X_1X_2$, $M_1M_2X_1X_2$, $M_1M_2M_3X_1X_2$, $M_1X_1X_2X_3$, $M_1M_2X_1X_2X_3$, and $M_1M_2M_3X_1X_2X_3$, where M_1, M_2, and M_3 are each selected from the group consisting of Zn, Cd, Hg, Al, Ga, In, Tl, Pb, Sn, Mg, Ca, Sr, and Ba, mixtures and alloys thereof and X_1, X_2, and X_3 are each selected from the group consisting of S, Se, Te, As, Sb, N, P; mixtures and alloys thereof, Si, Ge, Au, Ag, Co, Fe, Ni, Cu, Mn and alloys of Au, Ag, Co, Fe, Ni, Cu, Mn or alloy combinations thereof.	Page 4 line 5 through page 5 line 16.
6. The process of claim 1 wherein said colloidal nanocrystals are of PbSe.	Page 3 lines 5-6, page 6 lines 16-18, page 13 line 29 through page 14 line 4, page 15 line 18 through page 16 line 10.
7. The process of claim 6 wherein said colloidal nanocrystals have a volume loading of up to at least about 13 percent by volume within said solid composite.	In the claim.
8. The process of claim 1 wherein the solid composite including colloidal nanocrystals uniformly dispersed within a sol-gel host matrix is characterized by maintaining a major portion of photoluminescent quantum yield exhibited by the colloidal nanocrystals prior to incorporation into the sol-gel host matrix.	Page 6 line 24 through page 7 line 4; page 16, lines 5-7; page 17 lines 6-7.
9. The process of claim 1 wherein said amphiphilic polymer is modified poly(acrylic acid) or modified poly(methacrylic acid), said modified poly(acrylic acid) or modified poly(methacrylic acid) including hydrophobic regions.	Page 9 lines 10 though page 10 line 20; page 14 lines 20-21; page 15 lines 18-21; page 16 lines 12-13; page 16 line 26.
10. The process of claim 9 wherein said amphiphilic polymer is an octylamine-modified poly(acrylic acid).	Page 9 line 22 though page 10 line 2; page 10 lines 16-20; page 14 lines 20-21; page 15 lines 18-21; page 16 lines 12-13; page 16 lines 26-29.
11. The process of claim 1 wherein said sol-gel host is transparent.	In the claim.
12. The process of claim 1 wherein colloidal nanocrystals are uniformly dispersed within a sol-gel host.	In the claim.
13-16. (withdrawn)	
17. A solid composite comprising the reaction product of (i) colloidal nanocrystals complexed with an amphiphilic	Page 14 line 20 through page 17 line 7.

polymer including both hydrophobic groups and hydrophilic groups and (ii) a sol-gel precursor material.	
18. The solid composite of claim 17 wherein said colloidal nanocrystals have a volume loading of up to about 30 percent by volume within said solid state composite.	Page 12 line 24 through page 13 line 1.
19. The solid composite of claim 17 wherein said hydrophilic groups are selected from the group consisting of –COOH, -OH, $-SO_3H$, $-NH_2$, and $-PO_3H_2$.	Page 13 line 8-11.
20. The solid composite of claim 17 wherein the solid composite is characterized by maintaining a major portion of quantum yield exhibited by the colloidal nanocrystals prior to incorporation into the sol-gel precursor material.	Page 6 line 24 through page 7 line 4; page 16, lines 5-7; page 17 lines 6-7.
21. The solid colloidal composite of claim 17 wherein said colloidal nanocrystals are selected from the group consisting of M_1X_1, $M_1M_2X_1$, $M_1M_2M_3X_1$, $M_1X_1X_2$, $M_1M_2X_1X_2$, $M_1M_2M_3X_1X_2$, $M_1X_1X_2X_3$, $M_1M_2X_1X_2X_3$, and $M_1M_2M_3X_1X_2X_3$, where M_1, M_2, and M_3 are each selected from the group consisting of Zn, Cd, Hg, Al, Ga, In, Tl, Pb, Sn, Mg, Ca, Sr, and Ba, mixtures and alloys thereof and X_1, X_2, and X_3 are each selected from the group consisting of S, Se, Te, As, Sb, N, P; mixtures and alloys thereof, Si, Ge, Au, Ag, Co, Fe, Ni, Cu, Mn and alloys of Au, Ag, Co, Fe, Ni, Cu, Mn or alloy combinations thereof.	Page 4 line 5 through page 5 line 16.
22. The solid composite of claim 17 wherein the colloidal nanocrystals are of PbSe.	Page 3 lines 5-6, page 6 lines 16-18, page 13 line 29 through page 14 line 4, page 15 line 18 through page 16 line 10.
23. The solid composite of claim 17 wherein said amphiphilic polymer is modified poly(acrylic acid) or modified poly(methacrylic acid), said modified poly(acrylic acid) or modified poly(methacrylic acid) including hydrophobic groups.	Page 9 lines 10 though page 10 line 20; page 14 lines 20-21; page 15 lines 18-21; page 16 lines 12-13; page 16 line 26.
24. The solid composite of claim 23 wherein said amphiphilic polymer is octylamine-modified poly(acrylic acid).	Page 9 line 22 though page 10 line 2; page 10 lines 16-20; page 14 lines 20-21; page 15 lines 18-21; page 16 lines 12-13; page 16 lines 26-29.
25. The solid composite of claim 17 wherein said sol-gel	Page 12 lines 9-15.

precursor material is selected from the group consisting of metal alkoxide compounds, metal halide compounds, and metal hydroxide compounds where the metal is selected from the group consisting of silicon, titanium, zirconium, aluminum, vanadium, iron, tin, tantalum, cerium, and chromium.	
26. The solid composite of claim 17 wherein said sol-gel precursor material is transparent.	In the claim.
27. The solid composite of claim 17 wherein said colloidal nanocrystals are uniformly dispersed within a sol-gel.	In the claim.

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1. Whether claims 1, 2, 4-9, 11-12, 17, 18, 20-23, and 25-27 were properly rejected under 35 U.S.C. §102(b) over U. S. Patent Application Publication 2002/0110180 to Barney et al. ("Barney").

2. Whether claims 11, 12, 26, and 27 were properly rejected under 35 U.S.C. §103(a) as obvious over Barney.

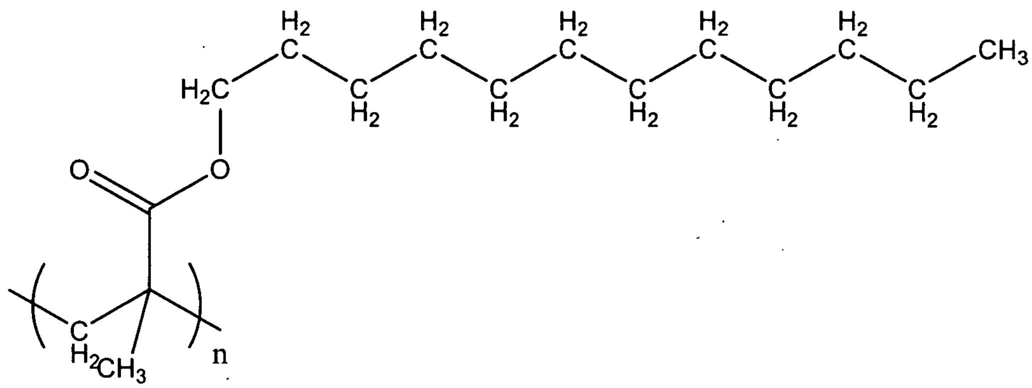
3. Whether claims 3, 10, 19, and 24 were properly rejected under 35 U.S.C. §103(a) as being unpatentable over Barney in view of U.S. Patent Application Publication 2002/155507 to Bruchez et al. ("Bruchez").

ARGUMENT

1. Claims 1, 2, 4-9, 11-12, 17, 18, 20-23, and 25-27 were rejected under 35 U.S.C. §102(b) as being anticipated by Barney. For a proper rejection under 35 U.S.C. §102(b), the cited prior art must teach all of the claimed limitations. The rejection of claims 1, 2, 4-9, 11-12, 17, 18, 20-23, and 25-27 under 35 U.S.C. §102(b) is improper because Barney does not teach all of the claimed limitations.

2. With regards independent claim 1, the Office Action argues that Barney teaches colloidal nanocrystals and a process of making a solid composite including nanocrystals by mixing nanocrystals with an amphiphilic material and a sol-gel precursor. The Office Action cites Barney at paragraphs [0015] and [0022] as a disclosure of "an amphiphilic material".

3. Appellant respectfully disagrees with the Office Action because Appellant's claimed process is for admixing colloidal nanocrystals specifically with an amphiphilic <u>polymer</u> having hydrophobic groups and hydrophilic groups, but Barney is silent with regard to an amphiphilic polymer. Neither paragraph [0015] nor paragraph [0022], cited by the Office Action, describes or teaches an amphiphilic polymer. Paragraph [0015] mentions poly(lauryl methacrylate) as a matrix for ZnS-capped CdSe nanocrystals. Anyone of average skill in the art would know from the structure that poly(lauryl methyacrylate) is <u>not</u> an <u>amphiphilic</u> polymer. Poly(lauryl methylacrylate), which has the structure



includes a hydrophobic backbone and hydrophobic side chains. This polymer is not an amphiphilic polymer having both hydrophobic groups and hydrophilic groups because it does <u>not</u> contain <u>hydrophilic</u> groups. The long chain attached to the polymer backbone is hydrophobic, not hydrophilic. The Office Action argues that Barney teaches amphiphilic *materials* such as alkyl phosphines, alkyl phosphine oxides, alkyl phosphonic acids, or alkyl phosphinic acids such as tri-n-octyl phosphine and tri-n-octyl phosphine. Barney at paragraph [0023] cites these materials as typical coordinating <u>solvents</u> that help control the growth of nanocrystals. <u>None</u> of these materials is an amphiphilic polymer. Barney mentions briefly in paragraph [0011] that the nanocrystals can be coated with an organic or organometallic overlayer to make the nanocrystals dispersible in a binder. Barney also mentions in paragraph [0030] that the overlayer can have reactive groups that can react with another compound to bond the nanocrystals to the binder, which can form a matrix that can be "an organic polymer matrix such as a

polyacrylate matrix or an inorganic matrix such as a sol-gel derived matrix". Barney's only example of a polyacrylate matrix is poly(lauryl methylacrylate) cited by the Office Action. This matrix, as Appellant has explained, is not an amphiphilic polymer. Further, Barney teaches that the matrix could be either this polymer or a sol-gel matrix. Thus, although Barney contemplates that the matrix could be a sol-gel matrix, Barney does not teach that the matrix could be a sol-gel matrix in combination with an amphiphilic polymer. For these reasons, Barney does not anticipate claim 1. Therefore, the rejection of claim 1 under 35 U.S.C. §102(b) over Barney is improper.

4. Claims 2, 4-9, and 11-12 depend directly or indirectly from claim 1 and therefore also include the step of admixing the nanocrystals with an amphiphilic polymer. Barney is silent with regard to admixing nanocrystals with an amphiphilic polymer. Moreover, Barney does not teach amphiphilic polymers. Thus, Barney does not anticipate claims 2-12. Therefore, the rejections of claims 2, 4-9, 11-12 under 35 U.S.C. §102(b) over Barney are also improper.

5. Further with regards to claim 6, Barney does not specifically disclose a process of preparing a solid composite of PbSe colloidal nanocrystals dispersed within a sol-gel host matrix by admixing PbSe nanocrystals with an amphiphilic polymer to form to alcoholic-soluble colloidal PbSe-amphiphilic polymer complex, and then admixing the PbSe-amphiphilic polymer complex with a sol-gel precursor material, and then forming the solid composite from the admixture of the PbSe-amphiphilic polymer and sol-gel precursor. Furthermore, the process of claim 6 produced PbSe films that lase in the infrared region. This demonstration of unexpected results is set forth in Example 2 of the specification, where tunable amplified spontaneous emission (ASE) was obtained from a solid composite prepared by the claimed method of forming a complex of PbSe nanocrystals with an amphiphilic polymer of an octylamine-modified poly(acrylic acid). The prior lack of success for achieving lasing in the near-IR region with nanocrystalline salts was noted in the Jacoby reference and the Borman references. Appellant's process provides the PbSe-containing product wherein successful lasing is achieved.

For these additional reasons, claim 6 is not anticipated by Barney, nor is claim 6 obvious in view of Barney.

6. Further with regards to claim 7, Barney does not specifically disclose a process of preparing a solid composite of PbSe colloidal nanocrystals dispersed within a sol-gel host matrix by admixing PbSe nanocrystals with an amphiphilic polymer to form to alcoholic-soluble colloidal PbSe-amphiphilic polymer complex, and then admixing the PbSe-amphiphilic polymer complex with a sol-gel precursor material, and then forming the solid composite from the admixture of the PbSe-amphiphilic polymer and sol-gel precursor wherein the PbSe nanocrystals have a volume loading of up to at least about 13 percent by volume within the solid composite. Additionally, claim 7 depends from claim 6, and Appellant has explained in the previous paragraph that the process of claim 6 produces a PbSe product that unexpectedly lases in the near IR region. For these additional reasons, Barney does not anticipate claim 7, and Barney does not render obvious claim 7.

7. Further with regards to claim 9, Barney does not teach an amphiphilic polymer of "modified poly(acrylic acid) or modified poly(methacrylic acid)". For this additional reason, Barney does not anticipate claim 9.

8. With regards to independent claim 17, Appellant respectfully disagrees with the Office Action because Barney does not teach Appellant's claimed solid composite because (i) Barney does not teach a complex between nanocrystals and an amphiphilic polymer, (ii) Barney does not teach a reaction product between the complex and a sol-gel precursor, and (iii) Barney is silent with regard to an amphiphilic polymer. Thus, Barney does not anticipate claim 17. Therefore, the rejection of claim 17 under 35 U.S.C. §102(b) over Barney is improper.

9. Claims 18, 20-23, and 25-27 depend directly or indirectly from claim 17 and therefore include all of the limitations of claim 17. Barney does not teach Appellant's claimed solid composite because (i) Barney does not teach a complex between

nanocrystals and an amphiphilic polymer, (ii) Barney does not teach a reaction product between the complex and a sol-gel precursor, and (iii) Barney is silent with regard to an amphiphilic polymer. Thus, Barney does not anticipate claims 18-23 and 25-27 under 35 U.S.C. 102(b). Therefore, the rejections of claims 18-23 and 25-27 under 35 U.S.C. 102(b) are improper.

10. Further with regards to claim 22, Barney does not specifically teach a solid composite specifically of PbSe nanocrystals that is the reaction product of (i) colloidal PbSe nanocrystals complexed with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups and (ii) a sol-gel precursor material. Furthermore, the PbSe films produced by the product unexpectedly lase in the infrared region. This demonstration of unexpected results is set forth in Example 2 of the specification, where tunable amplified spontaneous emission (ASE) was obtained from a solid composite prepared by the claimed method of forming a complex of PbSe nanocrystals with an amphiphilic polymer of an octylamine-modified poly(acrylic acid). The prior lack of success for achieving lasing in the near-IR region with nanocrystalline salts was noted in the Jacoby reference and the Borman references. Appellant's process provides the PbSe-containing product wherein successful lasing is achieved. For these additional reasons, Barney does not anticipate claim 22, and Barney does not render claim 22 obvious.

11. Further with regards to claim 23, Barney does not teach “modified poly(acrylic acid) or modified poly(methacrylic acid)”. For this additional reason, Barney does not anticipate claim 23.

12. Further with regards to claim 24, Barney does not teach octylamine-modified poly(acrylic acid). For this additional reason, Barney does not anticipate claim 24.

13. Claims 11, 12, 26, and 27 were rejected under 35 U.S.C. 103(a) as being obvious over Barney. For a proper rejection under 35 U.S.C. §103(a), the Office Action

must first show that the combined cited prior art render the claimed invention *prima facie* obvious. The Office Action has not yet met this burden.

14. Claims 11, 12 are not *prima facie* obvious in view of Barney because claims 11 and 12 depend from claim 1 and Barney does not disclose all of the steps of Appellant's claim 1. For example, Barney does not disclose Appellant's claimed step of admixing nanocrystals with an amphiphilic polymer having hydrophobic groups and hydrophilic groups. Thus, Barney does not render claims 11 and 12 *prima facie* obvious. Therefore, the rejection of claims 11 and 12 under U.S.C. §103(a) is improper. Claims 26 and 27 depend from claim 17. Barney does not disclose the a reaction product between (i) a complex of nanocrystals and amphiphilic polymer having both hydrophilic and hydrophobic groups with (ii) a sol-gel precursor material. Therefore, the rejection of claims 26 and 27 under U.S.C. §103(a) is improper.

15. Claims 3, 10, 19, and 24 were rejected under 35 U.S.C. 103(a) as being unpatentable over Barney in view of U.S. Patent Application Publication 2002/155507 to Bruchez et al. ("Bruchez"). The Office Action argues that:

(i) Barney teaches colloidal nanocrystals, a solid composite including nanocrystals and a process of making a solid composite including nanocrystals comprising mixing nanocrystals with an amphiphilic material and a sol-gel precursor and forming a solid matrix;

(ii) Barney does not disclose expressly the use of octylamine-modified poly(acrylic acid) as an amphiphilic polymer;

(iii) Bruchez at paragraph [0287] discloses semi-conductor nanocrystals produced with partially grafted (acrylic acid) in which octylamines were attached to about 40% of the carboxyl groups of the poly(acrylic acid); and therefore

(iv) At the time of the invention, it would have been obvious to a person of ordinary skill in the art to use the octylamine-modified poly(acrylic acid) polymer of Bruchez in the compositions and processes of Barney.

16. Appellant respectfully disagrees with the Office Action. Applicant submits that when a person of ordinary skill in the art considers the teachings of Barney as a whole along with the teachings of Bruchez as a whole, that person of ordinary skill in the art would not be motivated to combine the teachings of Barney with those of Bruchez in the manner disclosed by the Office Action. Barney, as a whole, is about temperature sensors, temperature sensing, and about using nanocrystals for the purposes of sensing temperature (i.e. Barney is making a thermometer of nanocrystals). Bruchez is not about temperature sensors. Rather, Bruchez as a whole is about is about labeling cells with SCNCs (semiconducting nanocrystals) and then screening the labeled cells. Barney shows how a composition of colloidal nanocrystals of ZnS-capped CdSe in a poly(lauryl methylacrylate) matrix produces a luminescence intensity that is different at various temperatures. Barney describes how to make a temperature sensor by applying a compositions to a surface as a paint or a film. Barney never mentions that these surfaces could be, for example, a cell membrane. Bruchez, on the other hand, is concerned with labeling cells with nanocrystals so that the cells can be screened. Bruchez is silent with respect to temperature sensing. Thus, Barney as a whole is about temperature sensing. Bruchez as a whole, on the other hand, is about labeling cells with SCNCs (semiconducting nanocrystals) and then screening the labeled cells. Both Barney and Bruchez use nanocrystals but in completely different ways. For these reasons, Applicant submits that claims 3, 10, 19, and 24 are not rendered obvious by Barney in view of Bruchez. Furthermore, Barney and Bruchez teach different chemical methods. Barney is silent with regard to any chemical methods employing amphiphilic polymers. Although Bruchez uses partially grafted (acrylic acid) in which octylamines were attached to about 40% of the carboxyl groups of the poly(acrylic acid), as the Office Action correctly points out, the question becomes: why would one or ordinary skill in the art choose this specific amphiphilic polymer in combination with Barney's teachings when Barney is silent with regard any amphiphilic polymer? In addition, Barney is silent with using an amphiphilic material in combination with a sol-gel precursor. Why would anyone of average skill in the art review Barney and Bruchez and conclude that this particular amphiphilic polymer should be combined first with

nanocrystals to form an alcohol soluble complex, and then react the complex with a sol-gel precursor material? Bruchez describes water-soluble complexes, but is silent with regard to alcohol-soluble complexes. For the above reasons, Applicant submits that the cited references provide no motivation or suggestion to one of ordinary skill in the art to apply the specific teachings of Barney and Bruchez in the manner described by the Office Action. Therefore the rejection of claims 3, 10, 19, and 24 under 35 U.S.C. 103(a) over Barney in view of Bruchez is improper.

17. In summary, Appellant submits that claims 1-9, 11-12, 17-23, and 25-27 are patentable over Barney, and that claims that claims 10 and 24 are patentable over Barney in view of Bruchez. Therefore, Appellant urges that the rejections to the claims be reversed.

Respectfully submitted,

Date: January 16, 2008

Samuel L. Borkowsky

Signature of Agent

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APPENDIX A - CLAIMS ON APPEAL

1. A process of preparing a solid composite including colloidal nanocrystals dispersed within a sol-gel host matrix, the process comprising:

admixing colloidal nanocrystals with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups within a solvent to form an alcoholic-soluble colloidal nanocrystal-polymer complex;

admixing the alcohol-soluble colloidal nanocrystal-polymer complex and a sol-gel precursor material; and,

forming said solid composite from said admixture.

2. The process of claim 1 wherein said colloidal nanocrystals have a volume loading of up to about 30 percent by volume within said solid composite.

3. The process of claim 1 wherein said hydrophilic groups are selected from the group consisting of –COOH, -OH, $-SO_3H$, $-NH_2$, and $–PO_3H_2$.

4. The process of claim 1 wherein said sol-gel precursor material is selected from the group consisting of metal alkoxide compounds, metal halide compounds, and metal hydroxide compounds where the metal is selected from the group consisting of silicon, titanium, zirconium, aluminum, vanadium, iron, tin, tantalum, cerium, and chromium.

5. The process of claim 1 wherein said colloidal nanocrystals are selected from the group consisting of M_1X_1, $M_1M_2X_1$, $M_1M_2M_3X_1$, $M_1X_1X_2$, $M_1M_2X_1X_2$, $M_1M_2M_3X_1X_2$, $M_1X_1X_2X_3$, $M_1M_2X_1X_2X_3$, and $M_1M_2M_3X_1X_2X_3$, where M_1, M_2, and M_3 are each selected from the group consisting of Zn, Cd, Hg, Al, Ga, In, Tl, Pb, Sn, Mg, Ca, Sr, and Ba, mixtures and alloys thereof and X_1, X_2, and X_3 are each selected from the group consisting of S, Se, Te, As, Sb, N, P; mixtures and alloys thereof, Si, Ge, Au, Ag, Co, Fe, Ni, Cu, Mn and alloys of Au, Ag, Co, Fe, Ni, Cu, Mn or alloy combinations thereof.

6. The process of claim 1 wherein said colloidal nanocrystals are of PbSe.

7. The process of claim 6 wherein said colloidal nanocrystals have a volume loading of up to at least about 13 percent by volume within said solid composite.

8. The process of claim 1 wherein the solid composite including colloidal nanocrystals uniformly dispersed within a sol-gel host matrix is characterized by maintaining a major portion of photoluminescent quantum yield exhibited by the colloidal nanocrystals prior to incorporation into the sol-gel host matrix.

9. The process of claim 1 wherein said amphiphilic polymer is modified poly(acrylic acid) or modified poly(methacrylic acid), said modified poly(acrylic acid) or modified poly(methacrylic acid) including hydrophobic regions.

10. The process of claim 9 wherein said amphiphilic polymer is an octylamine-modified poly(acrylic acid).

11. The process of claim 1 wherein said sol-gel host is transparent.

12. The process of claim 1 wherein colloidal nanocrystals are uniformly dispersed within a sol-gel host.

13-16. (withdrawn)

17. A solid composite comprising the reaction product of (i) colloidal nanocrystals complexed with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups and (ii) a sol-gel precursor material.

18. The solid composite of claim 17 wherein said colloidal nanocrystals have a volume loading of up to about 30 percent by volume within said solid state composite.

19. The solid composite of claim 17 wherein said hydrophilic groups are selected from the group consisting of –COOH, -OH, $-SO_3H$, $-NH_2$, and $–PO_3H_2$.

20. The solid composite of claim 17 wherein the solid composite is characterized by maintaining a major portion of quantum yield exhibited by the colloidal nanocrystals prior to incorporation into the sol-gel precursor material.

21. The solid colloidal composite of claim 17 wherein said colloidal nanocrystals are selected from the group consisting of M_1X_1, $M_1M_2X_1$, $M_1M_2M_3X_1$, $M_1X_1X_2$, $M_1M_2X_1X_2$, $M_1M_2M_3X_1X_2$, $M_1X_1X_2X_3$, $M_1M_2X_1X_2X_3$, and $M_1M_2M_3X_1X_2X_3$, where M_1, M_2, and M_3 are each selected from the group consisting of Zn, Cd, Hg, Al, Ga, In, Tl, Pb, Sn, Mg, Ca, Sr, and Ba, mixtures and alloys thereof and X_1, X_2, and X_3 are each selected from the group consisting of S, Se, Te, As, Sb, N, P; mixtures and alloys thereof, Si, Ge, Au, Ag, Co, Fe, Ni, Cu, Mn and alloys of Au, Ag, Co, Fe, Ni, Cu, Mn or alloy combinations thereof.

22. The solid composite of claim 17 wherein the colloidal nanocrystals are of PbSe.

23. The solid composite of claim 17 wherein said amphiphilic polymer is modified poly(acrylic acid) or modified poly(methacrylic acid), said modified poly(acrylic acid) or modified poly(methacrylic acid) including hydrophobic groups.

24. The solid composite of claim 23 wherein said amphiphilic polymer is octylamine-modified poly(acrylic acid).

25. The solid composite of claim 17 wherein said sol-gel precursor material is selected from the group consisting of metal alkoxide compounds, metal halide compounds, and metal hydroxide compounds where the metal is selected from the group consisting of silicon, titanium, zirconium, aluminum, vanadium, iron, tin, tantalum, cerium, and chromium.

26. The solid composite of claim 17 wherein said sol-gel precursor material is transparent.

27. The solid composite of claim 17 wherein said colloidal nanocrystals are uniformly dispersed within a sol-gel.

APPENDIX B
EVIDENCE

1. U.S. Patent Application Publication 2002/0110180 (“Barney”)

2. U.S. Patent Application Publication 2002/0155507 (“Bruchez”)

3. Jacoby, Optical Materials, December 1, 2003, volume 81, number 48, 3 pages ("Jacoby").

4. Borman, Chemical and Engineering News, December 22, 2003, vol. 81, number 51, 6 pages {“Borman”).

5. Schaller et al., "Tunable Near-Infrared Optical Gain and Amplified Spontaneous Emission Using PbSe Nanocrystals," J. Phys. Chem. B 2003, vol. 107, pp. 13765-13768 ("Shaller")

3. CLAIM COMPARISON WITH REJECTION

Claim limitation	Office Action's comment	Reference citation	Appellant's comment
1. A process of preparing a solid composite including colloidal nanocrystals dispersed within a sol-gel host matrix, the process comprising:	Barney teaches colloidal nanocrystals and a process for making a solid composite including nanocrystals.		Barney teaches colloidal nanocrystals and a process for making a solid composite including the nanocrystals.
admixing colloidal nanocrystals with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups within a solvent to form an alcoholic-soluble colloidal nanocrystal-polymer complex;	Barney teaches mixing nanocrystals with an amphiphilic material. Barney teaches amphiphilic materials because Barney discloses alkyl phosphines, alkyl phosphine oxides, alkyl phosphonic acids, or alkyl phosphinic acids such as tri-n-octyl phosphine and tri-n-octyl phosphine. Barney teaches poly(lauryl methacrylate).	The Office Action cites Barney paragraphs [0011] and [0022]. The Office Action cites Barney paragraph [0022] The Office Action cites paragraph [0015]	Barney does not admixing nanocrystals with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups within a solvent to form an alcoholic-soluble colloidal nanocrystal complex because Barney does not teach amphiphilic polymers. Barney recites alkyl phosphines, alkyl phosphine oxides, alkyl phosphonic acids, or alkyl phosphinic acids such as tri-n-octyl phosphine and tri-n-octyl phosphine as solvents. None of these materials is an amphiphilic polymer. Poly(lauryl methacrylate) is not an amphiphilic polymer because it lacks the hydrophilic groups.
admixing the alcohol-soluble colloidal nanocrystal-polymer complex and a sol-gel precursor material; and,	Barney teaches a sol-gel precursor	The Office Action cites Barney paragraph [0031] and [0018]	Barney does not teach forming the alcohol-soluble colloidal nanocrystal-polymer complex, therefore Barney does not recite admixing this complex with a sol-gel precursor.

forming said solid composite from said admixture.	Barney teaches forming a solid matrix containing the nanocrystals	The Office Action cites Barney paragraph [0031]	Barney does not teach the admixture and therefore does not teach forming the solid composite from the admixture.
6. The process of claim 1 wherein said colloidal nanocrystals are of PbSe.	Barney anticipates claim 6.		Barney does not anticipate the claim because claim 6 depends from claim 1, therefore including admixing nanocrystals with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups within a solvent to form an alcoholic-soluble colloidal nanocrystal complex (Barney does not teach amphiphilic polymers). Claim 1 also includes admixing this complex with a sol-gel precursor, however Barney does not teach forming the claimed complex. Barney also does not anticipate claim 6 because Barney does not specifically disclose a process of preparing a solid composite of PbSe colloidal nanocrystals dispersed within a sol-gel host matrix by admixing PbSe nanocrystals with an amphiphilic polymer to form to alcoholic-soluble colloidal PbSe-amphiphilic polymer complex, and then admixing the PbSe-amphiphilic polymer complex with a sol-gel precursor material, and then forming the solid composite from the admixture of the PbSe-amphiphilic polymer and sol-gel precursor wherein the PbSe nanocrystals have a volume loading of up to at least about 13

			percent by volume within the solid composite.
7. The process of claim 6 wherein said colloidal nanocrystals have a volume loading of up to at least about 13 percent by volume within said solid composite.	Barney anticipates claim 7.		Barney does not anticipate claim 7 because Barney does not specifically disclose a process of preparing a solid composite of PbSe colloidal nanocrystals dispersed within a sol-gel host matrix by admixing PbSe nanocrystals with an amphiphilic polymer to form to alcoholic-soluble colloidal PbSe-amphiphilic polymer complex, and then admixing the PbSe-amphiphilic polymer complex with a sol-gel precursor material, and then forming the solid composite from the admixture of the PbSe-amphiphilic polymer and sol-gel precursor wherein the PbSe nanocrystals have a volume loading of up to at least about 13 percent by volume within the solid composite.
17. A solid composite comprising the reaction product of (i) colloidal nanocrystals complexed with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups and (ii) a sol-gel precursor material.	Barney teaches mixing nanocrystals with an amphiphilic material.	The Office Action cites Barney paragraphs [0011] and [0022].	Barney does not admixing nanocrystals with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups within a solvent to form an alcoholic-soluble colloidal nanocrystal complex because Barney does not teach amphiphilic polymers.
	Barney teaches amphiphilic materials because Barney discloses alkyl phosphines, alkyl phosphine oxides, alkyl	The Office Action cites Barney paragraph [0022]	Barney recites alkyl phosphines, alkyl phosphine oxides, alkyl phosphonic acids, or alkyl phosphinic acids such as tri-n-

	phosphonic acids, or alkyl phosphinic acids such as tri-n-octyl phosphine and tri-n-octyl phosphine. Barney teaches poly(lauryl methacrylate).	The Office Action cites paragraph [0015]	octyl phosphine and tri-n-octyl phosphine as solvents. None of these materials is an amphiphilic polymer. Poly(lauryl methacrylate) is not an amphiphilic polymer because it lacks the hydrophilic groups. Barney does not teach a complex between nanocrystals and an amphiphilic polymer. Barney does not teach a reaction product between the complex and a sol-gel precursor. Barney is <u>silent</u> with regard to an amphiphilic polymer. Thus, Barney does not anticipate claim 17.
22. The solid composite of claim 17 wherein the colloidal nanocrystals are of PbSe.	Barney anticipates claim 22.		Barney does not anticipate claim 22 because claim 22 depends from claim 17, and Barney does not anticipate claim 17 for the reasons cited above. Furthermore, Barney does not specifically teach a solid composite specifically of PbSe nanocrystals that is the reaction product of (i) colloidal PbSe nanocrystals complexed with an amphiphilic polymer including both hydrophobic groups and hydrophilic groups and (ii) a sol-gel precursor material. For this additional reason, Barney does not anticipate claim 22.

APPENDIX C
RELATED PROCEEDINGS

None.

TODAY'S HEADLINES

December 1, 2003
Volume 81, Number 48
CENEAR 81 48 p. 7
ISSN 0009-2347

OPTICAL MATERIALS

TUNABLE IR LASERS FROM QUANTUM DOTS

Novel synthesis yields nanocrystalline PbSe films that lase in near-infrared

MITCH JACOBY

Tunable infrared lasers based on nanocrystals may become available soon. Researchers at Los Alamos National Laboratory in New Mexico have shown that amplified spontaneous emission--an important milestone along the road to making practical lasers--can be achieved in the near-IR region using nanocrystalline lead salts. The advance may be especially useful in optical telecommunications, remote sensing, and related applications that depend upon light in that wavelength region.

Chemical flexibility and ease of processing make nanometer-sized semiconductor crystals (quantum dots) ideal candidate materials for numerous applications involving light emission. A number of proposed applications, such as luminescent markers for biological assays and lasers and optical amplifiers for visible light, have been developed or demonstrated to be feasible. But efforts to generate infrared laser light using nanocrystals have been unsuccessful until now. And the lack of success had begun to convince some researchers that the goal was unlikely to be attained because of fundamental limitations.

LASER PROS Los Alamos scientists (from left) Schaller, Petruska, and Klimov.
PHOTO BY JOSHUA E. SMITH

But now, Los Alamos postdoctoral fellows Richard D. Schaller and Melissa A. Petruska and team leader Victor I. Klimov have demonstrated that a novel synthesis procedure for preparing lead selenide nanocrystals in a titania matrix leads to high-quality optical films capable of generating amplified spontaneous emission in the near-IR region [*J. Phys. Chem. B*, published online Nov. 21, http://dx.doi.org/10.1021/jp0311660].

"It's an important advance, especially for technological applications," says Alexander Efros, a staff scientist at the Naval Research Laboratory in Washington, D.C. By adjusting the size of nanocrystals synthetically, scientists can tune the light emitted from quantum dot sources, Efros explains. That type of flexibility should make it possible to adjust the output of future optical devices so that scattering and absorption interferences can be avoided.

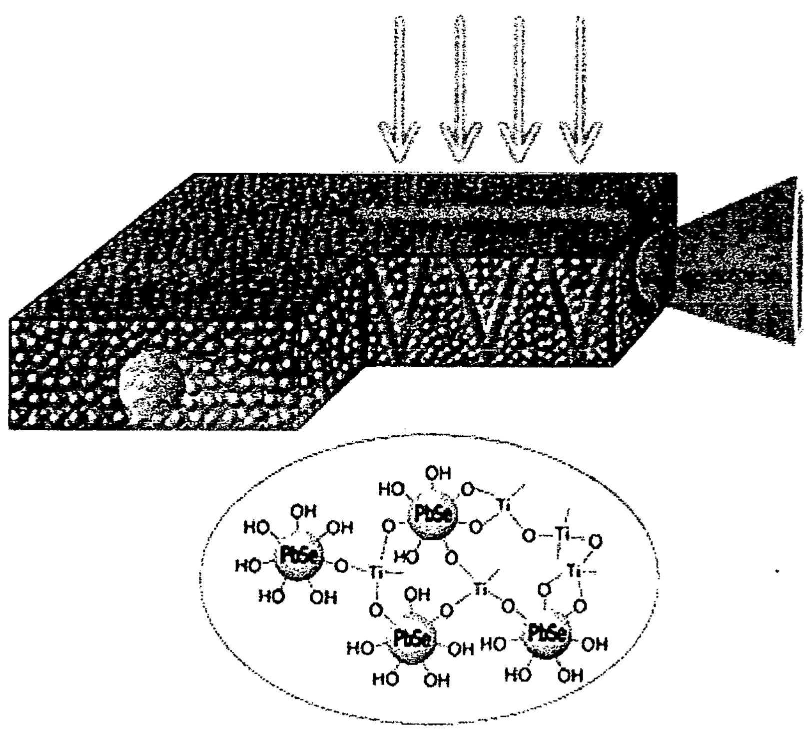
Three years ago, the Los Alamos group and their coworkers reported that CdSe nanocrystals

could be made to lase in the visible region (C&EN, Oct. 23, 2000, page 78). Motivated by this success, the Los Alamos team and other research groups sought to use nanocrystals of lead salts to produce IR laser light. But despite some indications that lead-based nanocrystals could work in that application, the lasing effect remained elusive.

Two fundamental shortcomings make it difficult to achieve lasing in PbSe. One of the problems is that several of PbSe's lowest electronic states have equivalent (degenerate) energy levels. In addition, excitations that potentially could lead to IR emission can be quenched rapidly by a fast competing process known as Auger recombination, which does not lead to light emission.

"The nonradiative mechanism steals energy from the lasing transition," explains Mark I. Stockman, a physics professor at Georgia State University, Atlanta. Stockman adds that despite these problems, the Los Alamos group has shown via "a direct and convincing demonstration" that lasing is still possible and can be achieved in a practical manner.

Klimov and coworkers credit their synthesis method, which includes colloidal chemistry techniques and amphiphilic polymers, with producing optical films of high enough quality to observe the lasing effect. According to the Los Alamos group, the results indicate that the lack of success previously in developing the required lasing conditions in nanocrystalline lead salts was due to material quality issues, not intrinsic physical limitations.



SHINE ON Irradiating films of lead selenide nanocrystals (yellow spheres) embedded in a matrix made from titania and an amphiphilic polymer triggers lasing action that produces amplified IR light.
IMAGE BY JOSHUA E. SMITH

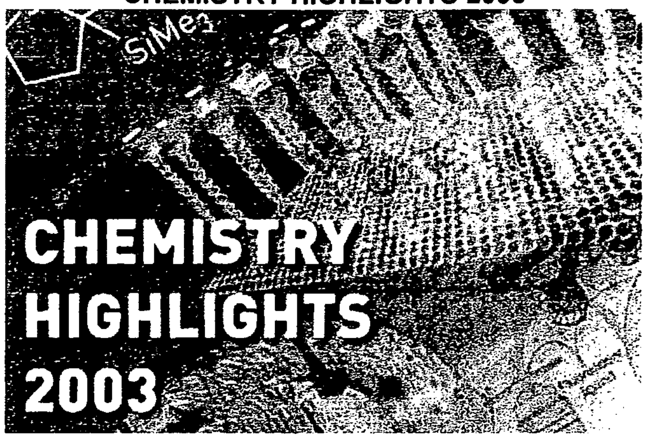
Top

CHEMICAL & Engineering News

COVER STORY

December 22, 2003
Volume 81, Number 51
CENEAR 81 51 pp. 39-50
ISSN 0009-2347

CHEMISTRY HIGHLIGHTS 2003



Key advances were reported this year across a broad span of chemistry subdisciplines, ranging from carbohydrate chemistry to surface science

STU BORMAN, C&EN WASHINGTON

A steady stream of news on the latest chemical research developments flows by us with dizzying speed all year, every year. In C&EN's annual Chemistry Highlights, we recall some of the impressive advances we've reported on during the year.

In selecting developments to be included in this year-end review, we look for studies that have an identifiably superlative quality or element of uniqueness--such as the first time something was done, an order-of-magnitude improvement, or a capability that was just not possible before.

Our list is meant to be representative, not comprehensive. So we're by no means implying that it's not important if it's not here.

Our hope is merely that our selections, when considered as a whole, help provide greater perspective on the enormous scientific and technical strides--and consequent benefits to society--made by the chemistry research enterprise each and every year.

Chemistry Highlights 2003

Cover Story

E-mail this article to a friend
Print this article
E-mail the editor

Top

Home | Table of Contents | Today's Headlines | Business | Government & Policy | Science & Technology | cen-chemjobs.org

About C&EN | How To Reach Us | How to Advertise | Editorial Calendar | Email Webmaster

Pubs Page / chemistry.org / ChemPort / CAS

COVER STORY

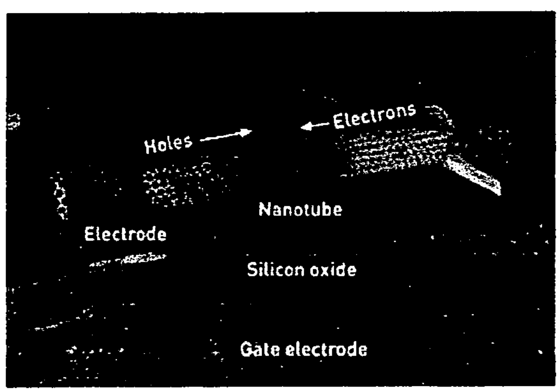
December 22, 2003
Volume 81, Number 51
CENEAR 81 51 pp. 39-50
ISSN 0009-2347

NANOTECH & MOLECULAR ELECTRONICS

STU BORMAN, C&EN WASHINGTON

Although the question of whether nanorobots can exist remains unresolved, progress nevertheless continues apace on a range of nanoscale techniques and molecular electronic devices.

The first nanoscale light source based on a single carbon nanotube (acting as a field-effect transistor) was demonstrated by Phaedon Avouris, James A. Misewich, Richard Martel, and coworkers at IBM's T. J. Watson Research Center, Yorktown Heights, N.Y. [*Science*, **300**, 783 (2003)]. An IBM group including Avouris, Martel, and Marcus Freitag also generated an electrical current in a single carbon nanotube by shining light on it [*Nano Lett.*, **3**, 1067 (2003)]. Both studies have implications for miniature photonic and optoelectronic devices.



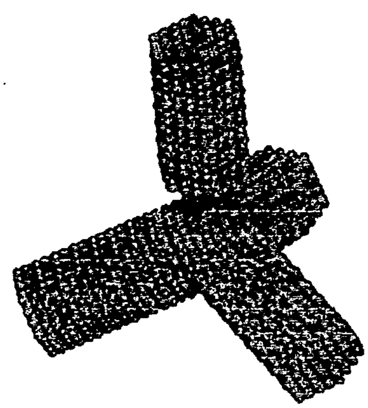
TOTALLY TUBULAR **By injecting charge carriers (holes and electrons) at opposite ends of a carbon nanotube, Avouris, Misewich, Martel, and coworkers at IBM produced polarized infrared light.** IBM T. J. WATSON RESEARCH CENTER PHOTO

A technique for changing nanotube electrical properties was devised by Robert C. Haddon and coworkers at the University of California, Riverside. They showed that functionalizing conductive metallic nanotubes with dichlorocarbene caused the nanotubes to take on semiconducting properties [*Science*, **301**, 1501 (2003)].

Michael S. Strano of the University of Illinois, Urbana-Champaign, James M. Tour and Richard E. Smalley of Rice University, and coworkers found this year that functionalizing nanotubes with diazonium reagents differentiates metallic and semiconducting single-walled carbon nanotubes and makes it possible to separate and manipulate them, based on differences in electronic structure [*Science*, **301**, 1519 (2003)]. And Ming Zheng of DuPont Central Research & Development, Wilmington, Del., and coworkers showed that certain sequences of DNA can wrap helically around single-walled carbon nanotubes and also permit them to be separated, based on optical features [*Science*, **302**, 1545 (2003)].

Victor I. Klimov and coworkers at Los Alamos National Laboratory showed that amplified spontaneous emission--an important step toward tunable IR lasers--can be achieved in the near-IR region using nanocrystals of lead salts [*J. Phys. Chem. B*, published online Nov. 21, http://dx.doi.org/10.1021/jp0311660].

In a moving development, the first nanometer-sized, electrically driven synthetic motor--a gold rotor and a multiwalled carbon nanotube axis on a silicon chip--was built by Alex Zettl and coworkers at the University of California, Berkeley, and Lawrence Berkeley National Laboratory [*Nature*, **424**, 408 (2003)].



NANOTETRAPOD These CdTe nanocrystals were created by Alivisatos and coworkers.
COURTESY OF A. PAUL ALIVISATOS

Four-armed CdTe nanocrystals made by A. Paul Alivisatos and coworkers at the University of California, Berkeley, and Lawrence Berkeley National Laboratory [*Nat. Mater.*, **2**, 382 (2003)] were described as "one of the best controlled nanocrystal systems with complex shapes." The nanocrystals could find use in solar cells or as polymer additives.

Molecular electronics display-related developments this year included a polymer-based electroluminescent device that can be switched

between glowing red or green by reversing the direction of current flow. It was produced by Luisa De Cola at the University of Amsterdam, Klemens Brunner at Philips Research Laboratories, Eindhoven, the Netherlands, and coworkers [*Nature*, **421**, 54 (2003)]. The device could simplify the fabrication and increase the brightness of displays, light sources, and color switches.

A new solution-processing method can be used to pattern red, green, and blue electroluminescent polymers with resolution that exceeds what's required for flat-screen, full-color organic light-emitting diode displays. Formerly, the resolution of wet-chemical patterning processes for electroluminescent polymers wasn't high enough to create such displays. The new method was developed by Klaus Meerholz at the University of Munich (now at the University of Cologne); Heinrich Becker of Covion Organic Semiconductors, Frankfurt; Oskar Nuyken at the Technical University of Munich; and coworkers [*Nature*, **421**, 829 (2003)].

A novel technique for aligning liquid crystals--developed by Roeland J. M. Nolte of the University of Nijmegen, the Netherlands, and coworkers--eliminates the current need for clean-room conditions in liquid-crystal display manufacture [*Angew. Chem. Int. Ed.*, **42**, 1812 (2003)].

Chemistry professor James R. Heath of California Institute of Technology and coworkers devised a method for producing ultrahigh-density arrays of aligned nanowires and nanowire circuits [Science, 300, 112 (2003)]. And a Technion–Israel Institute of Technology team led by Erez Braun and Kinneret Keren created a field-effect transistor by binding a single-wall carbon nanotube to a DNA strand and fabricating gold leads to the nanotube [*Science*, **302**, 1380 (2003)]. Techniques like this "will pave the way for integration of molecular components into useful microelectronics," a researcher commented.

In addition, many research teams are working to develop soft, flexible electronic technologies based on conducting fibers or organic thin-film materials. In one such study, Xiangfeng Duan and coworkers at Nanosys, in Medford, Mass., and Palo Alto, Calif., devised a low-cost, low-temperature process for fabricating high-performance thin-film transistors on flexible substrates [*Nature*, **425**, 274 (2003)]. The technology takes "nanoelectronics in a new direction," Duan tells C&EN, "exploiting nanomaterials not for electronic miniaturization, but for better and cheaper electronics over large areas."

Chemistry Highlights 2003

Top

Home | Table of Contents | Today's Headlines | Business | Government & Policy | Science & Technology | cen-chemjobs.org

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Tunable Near-Infrared Optical Gain and Amplified Spontaneous Emission Using PbSe Nanocrystals

R. D. Schaller, M. A. Petruska, and V. I. Klimov*

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Received: October 9, 2003

Here, for the first time, we demonstrate amplified spontaneous emission (ASE) from PbSe nanocrystals (NCs) with emission energies tunable in the near-infrared (IR). We show that despite complications associated with a high, 8-fold degeneracy of the lowest quantized states and fast, nonradiative Auger recombination, optical gain parameters of PbSe NCs are comparable to those of CdSe NCs used for light amplification in the visible. These results indicate that previous unsuccessful attempts to realize the lasing regime in NCs of lead salts were not due to intrinsic physical reasons but likely resulted from material quality issues. By using a novel sol–gel procedure that provides both good quality surface passivation and high NC filling factors (>15%), we fabricate PbSe NC/sol–gel nanocomposites that produce ASE, which is tunable via NC size, in the near-IR. This finding indicates the feasibility of NC-based amplifiers and lasers tunable in the near-IR range and, in particular, in the range of telecommunication windows.

Chemically synthesized nanocrystals (NCs) exhibit wide-range size-controlled tunability of the emission color and high photoluminescence (PL) quantum yields (QYs). These characteristics make NCs attractive materials for light-emitting applications ranging from bio-labeling[1] and solid-state lighting[2] to optical amplification and lasing.[3,4] Similar to such "soft" light emitters as organic dyes and conjugated polymers, colloidal NCs offer chemical flexibility and processibility and can be easily incorporated into photonic structures or optical waveguides.[5,6] However, while organic molecules are poor infrared (IR) light emitters, III–V[7] and IV–VI[8] NCs show efficient IR emission with high, up to near-unity QYs.[9] Here, we analyze the fundamental physics of light amplification in PbSe NCs with emission energies in the near-IR. We experimentally verify that the lowest quantized states of PbSe NCs exhibit a high, 8-fold degeneracy. We find that despite this high degeneracy and fast, nonradiative Auger recombination,[10,11] PbSe NCs exhibit optical gain parameters that are similar to those of CdSe NCs, which have been shown to produce light amplification at visible wavelengths.[3] Using a novel sol–gel procedure that maintains good surface passivation and high NC filling factors, we demonstrate size-tunable ASE from PbSe NC/sol–gel nanocomposites prepared in the form of "active" planar waveguides.

To date, light amplification and lasing have only been demonstrated for II–VI CdSe NCs.[3–6] However, because of the large energy gap (>1.75 eV), these NCs cannot be used for light amplification in the IR spectral range. On the other hand, tunable NC-based media capable of producing emission (see Figure 1a) and optical gain at a specific near- or mid-IR wavelength (within, e.g., telecommunication and atmospheric transparency windows) are highly desirable for a number of applications ranging from optical communications and remote sensing to a recent proposal of coherent plasmon generation.[12] Lead salts such as PbSe have been used as IR gain media in quantum-well-based devices.[13] Although previous studies of lead-salt NCs (PbS) dispersed in glass matrixes provided some indications of optical gain,[14] no evidence for the ASE regime was obtained. The existence of optical gain, however, does not ensure the development of ASE and laser action because of potentially hindering factors such as short gain lifetimes and/or strong optical losses that could lead to negative modal (i.e., net) gain despite the fact that the material gain (as measured, e.g., in ref 14) is positive.[3] The failure of all previous attempts to produce ASE using lead-based NCs resulted in the perception that fundamental physical issues prevent ASE and lasing regimes in these materials.

A review of PbSe properties may indeed lead to discouraging conclusions regarding the use of these materials for optical gain applications. One possible obstacle to the development of optical gain is associated with a multivalley character of the PbSe band structure [4 equivalent band minima at the L points of the Brillouin zone (Figure 1b)], which together with a 2-fold spin degeneracy, can lead to the 8-fold total degeneracy of NC quantized states involved in the "emitting" transition.[15] This high degeneracy, which we experimentally confirm below, directly impacts the optical gain threshold (i.e., the condition for the population inversion) by increasing it up to 4 electron–hole (e–h) pairs per NC on average instead of just 1 e–h pair in the case of 2-fold degeneracy.

Another potential complication is associated with highly efficient Auger recombination in which the e–h recombination energy is not released as a photon but is instead transferred to a third particle (an electron or a hole).[11] In bulk semiconductors, the Auger recombination rate increases exponentially as the energy gap is decreased.[16] Therefore, this process is much more efficient in narrow-band PbSe[17] than, e.g., in wide-gap CdSe, leading to a fast, subnanosecond carrier decay at excitation densities greater than 10^{18} cm^{-3}. In sub-10 nm PbSe NCs, the effective carrier densities are $> 10^{19}$ cm^{-3} in the case of just a few e–h pairs per NC, and hence Auger recombination can severely limit lifetimes of multi-e–h pair states that are responsible for producing optical gain.[18]

However, the above qualitative analysis is based upon properties of bulk PbSe and can only be indirectly related to PbSe NCs. To experimentally study optical gain properties of PbSe NCs, we use high-quality colloidal samples fabricated via

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10.1021/jp0311660 CCC: $25.00
Published on Web 11/21/2003

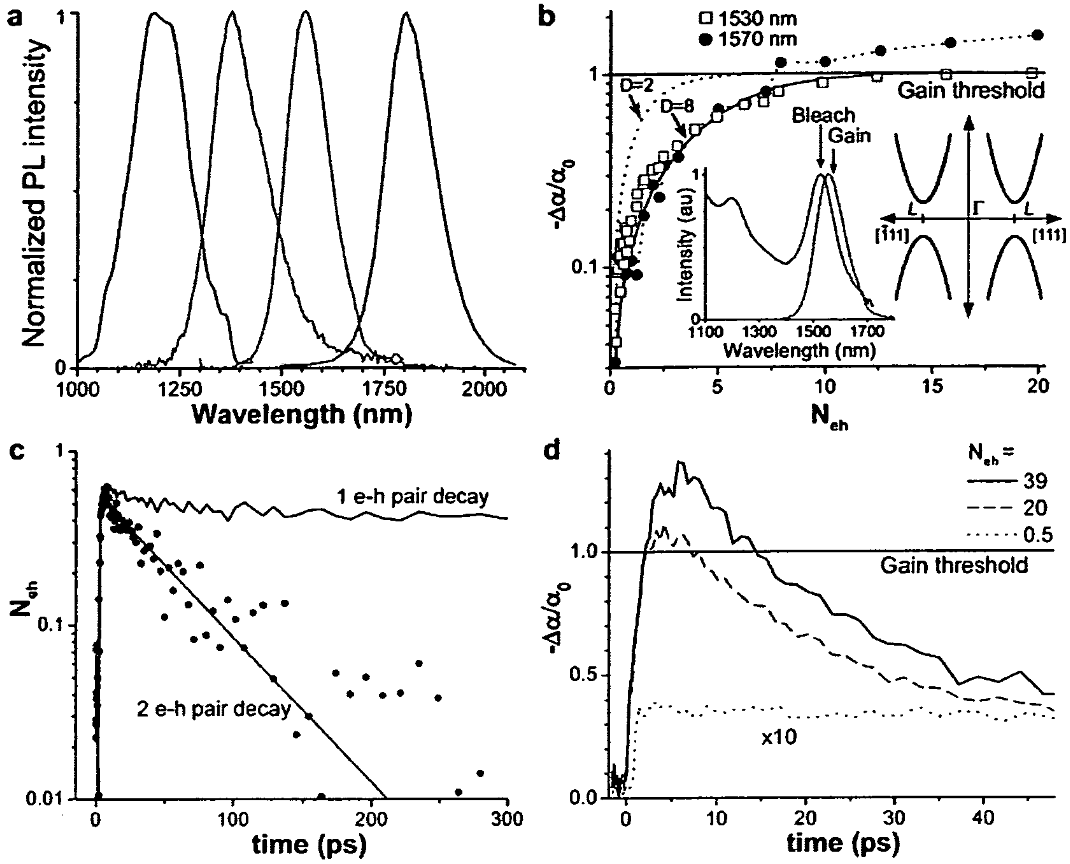

Figure 1. Optical properties of PbSe NC/hexane solutions. (a) The emission energies of PbSe NCs are size-tunable through the near-infrared with emission QYs of 70% (when compared to the IR laser dye IR26 and corrected for detector and diffraction grating efficiencies). (b) The pump-power dependent bleaching behavior of the A_1 band-edge absorption maximum (1530 nm) of PbSe NCs in hexane (squares) is closely reproduced by the Poisson distribution for NC populations in the case of the 8-fold degeneracy ($D = 8$) of states involved in the A_1 transition (solid line); this behavior differs significantly from that observed in the case of the 2-fold degeneracy ($D = 2$) (black dotted line) typical, e.g., for CdSe NCs.[19] The 4 equivalent band minima at L points of the Brillouin zone, which give rise to this 8-fold degeneracy, are shown schematically (inset). The pump-dependent bleaching at 1570 nm (circles) (~15 nm red-shifted from the PL band maximum) indicates a transition to optical gain ($-\Delta\alpha/\alpha > 1$) for excitation densities >8 e−h pairs/NC. (c) The high efficiency of Auger recombination is indicated by a direct comparison of the biexciton (circles) and single exciton (black line) decays. The biexciton decay is characterized by ~50 ps time constant, which is orders of magnitude faster than that for single excitons. (d) Highly efficient Auger recombination leads to the acceleration of the bleaching/gain decay (measured at 1570 nm) with increasing pump level. The gain lifetime measured at excitation densities corresponding to gain saturation (solid line) is ~10 ps.

an organometallic route[8] that show ~5% size dispersion and ~70% PL QY in hexane solutions. To detect optical gain and to monitor its dynamics, we use a transient absorption (TA) experiment in which the sample is excited by 50 fs, 1.55 eV pulses from an amplified Ti-sapphire laser, and the absorption change, $\Delta\alpha$, within the photoexcited spot is probed by variably delayed, 100 fs pulses from a tunable IR optical parametric amplifier. Optical gain corresponds to the situation for which the absorption bleaching is greater than the ground-state absorption, α_0, and hence that the absorption of the excited sample ($\alpha = \alpha_0 - |\Delta\alpha|$) is *negative*. As a measure of excitation densities, we use an average number of e−h pairs per NC, N_{eh}, generated by the pump pulse.

To evaluate the degeneracy of the lowest quantized levels in PbSe NCs and to estimate the "theoretical" gain threshold, we perform pump-induced absorption saturation measurements at the position of the band-edge absorption maximum (A_1). In Figure 1b, we compare the results of these measurements with saturation curves calculated for 2- and 8-fold degenerate states assuming the Poisson distribution of NC populations.[19] This comparison indicates that the degeneracy of the lowest NC levels is indeed 8 (as expected from the analysis above), suggesting that the gain threshold is 4 e−h pairs per NC. Further, this result shows that optical gain in PbSe NCs originates from high-order multiexcitonic states ($N_{eh} \geq 5$), which is in sharp contrast to CdSe NCs, for which the band-edge optical gain is dominated by well-defined biexcitonic ($N_{eh} = 2$) states (as a result of the 2-fold degeneracy of the lowest quantized levels).[18] Therefore, exciton−exciton interactions are expected to have a much stronger effect on the lasing performance of PbSe NCs in comparison with CdSe NCs via a strong influence on gain spectral and dynamical characteristics.

By monitoring TA signals below the A_1 absorption peak, we observe a gradual increase in $|\Delta\alpha|/\alpha_0$ with decreasing probe photon energy until it crosses unity, indicating a transition to optical gain (Figure 1b). Pump-dependent measurements of $|\Delta\alpha|$ (circles) at the gain spectral maximum (1570 nm) indicate that the gain threshold occurs at $N_{eh} \sim 8$, which is twice as high as the theoretical threshold, likely because of a competing contribution from excited state absorption as was previously observed for solutions of CdSe NCs.[20] However, despite being high in terms of the number of e−h pairs per NC, because of relatively large absorption cross sections, the "practical" threshold pump fluences for PbSe NCs are comparable to those for CdSe NCs and are ~0.1−1 mJ cm^{-2} per pulse. Furthermore, from the saturated gain magnitude (Figure 1b), we estimate that the gain cross section is ~2 × 10^{-15} cm^2, which is more than an order of magnitude greater than in CdSe NCs.[3]

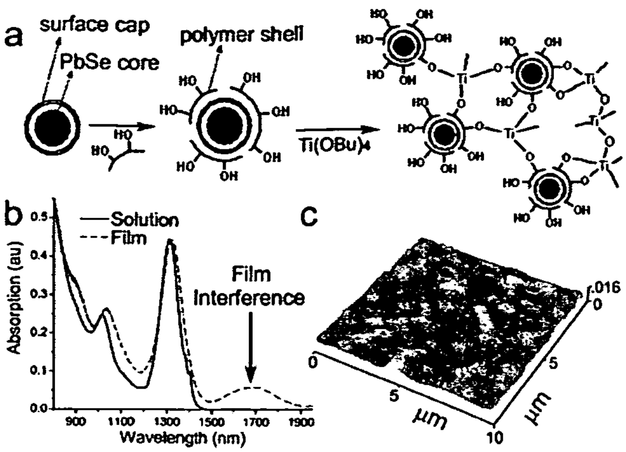

Figure 2. Sol-gel/NC synthetic route. (a) NCs are mixed with an amphiphilic polymer, which interacts with the NC surface and its capping ligands, forming a complex. The hydrophilic COOH groups (for clarity, only the OH reactive site of the COOH functionality is shown schematically) found on the exterior of this complex serve as the reactive sites through which the NCs are incorporated into the titania sol−gel matrix. (b) This chemistry, which can be generalized to other materials, allows the desirable optical properties of the NCs to be maintained when cast as high quality optical films, as can be seen in the reproducible absorption spectra of NCs before and after incorporation into the sol−gel film. (c) An atomic force microscopy image shows the high quality of the PbSe NC/sol−gel film with a height nonuniformity of <6 nm (much less than λ_{PL}).

To evaluate the role of multiexciton Auger recombination, we monitor pump-intensity dependent TA dynamics at both the A_1 absorption maximum (Figure 1c) and the gain band maximum (Figure 1d). Comparison of single e−h pair (exciton) and two e−h pair (biexciton) decays extracted from the A_1 bleaching dynamics[11] indicates that multiparticle interactions lead to a dramatic shortening of the biexciton lifetime ($\tau_2 \approx 50$ ps) compared to the single exciton lifetime. Strong multiparticle interactions directly affect optical gain dynamics (Figure 1d). At a low pump fluence ($N_{eh} < 1$), the $\Delta\alpha$ decay within the gain band is slow (consistent with single-exciton dynamics in Figure 1c), but it accelerates dramatically at pump fluences above the gain threshold for which nonradiative Auger recombination governs the decay of photoexcited carriers. The gain lifetime is ~10 ps at pump powers corresponding to gain saturation. Although quite short, this time is comparable to that observed in CdSe NCs.

The above results indicate that despite the fact that the physics of PbSe NCs seems to be unfavorable for optical gain applications, the measured optical gain parameters (gain threshold, cross section, and lifetime) are comparable or even superior to those in CdSe NCs. This observation indicates that previous failures in achieving ASE in lead-salt NCs have not been due to intrinsic "physical" reasons but were likely a result of insufficient material quality.

Two material parameters important for ASE performance are the quality of NC surface passivation and the concentration of NCs in the matrix/solvent. A sufficiently high degree of surface passivation is required to keep photoexcited carriers in the "gain-active" quantized states without being trapped at the surface for at least as long as the intrinsic, Auger-recombination-limited optical gain lifetime.[18] On the other hand, high NC volume fractions (practical threshold is a few percent[6]) are required to produce a fast buildup of the stimulated emission that "beats" the Auger decay. One approach that satisfies both conditions is the self-assembly of NCs into close packed solids.[3] Such solids maintain the high QYs achieved in solutions and also provide

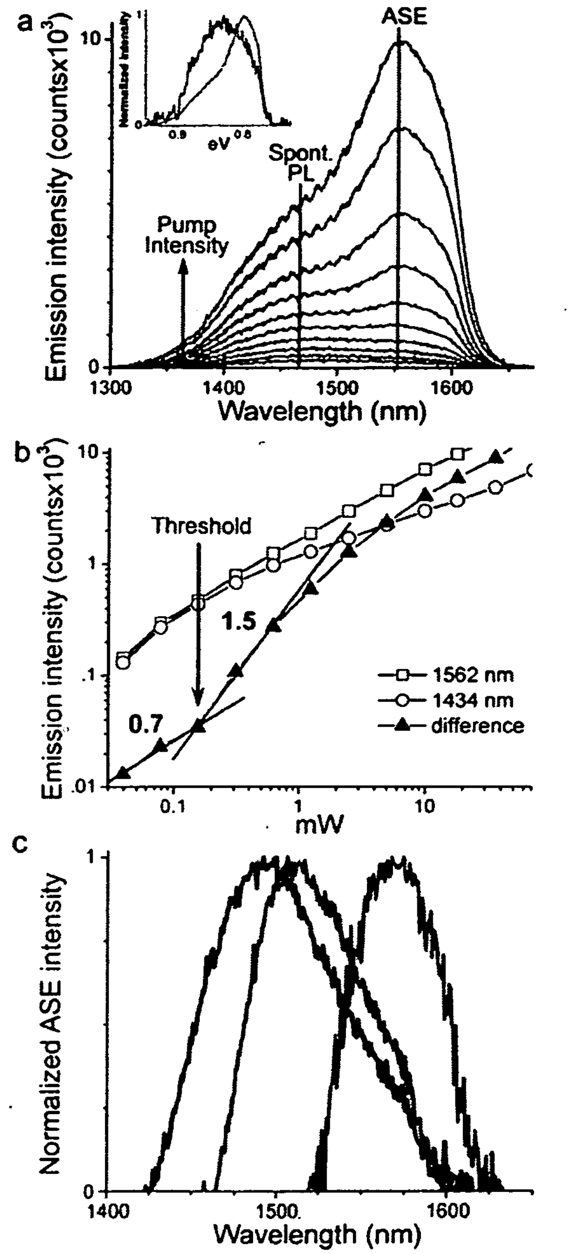

Figure 3. Amplified spontaneous emission in PbSe NCs. (a) Development of a spectrally narrowed ASE band at 1555 nm is observed as a function of pump power (100 Hz pump laser repetition rate) for a NC/sol−gel composite at $T = 80$ K. Comparison of normalized emission spectra produced using low (blue) and high (red) pump intensities (inset), which are dominated by spontaneous PL and ASE, respectively, shows the ASE as a spectrally narrowed, red-shifted band. The high-frequency modulation present in the spectra is an etalon artifact associated with the array detector. (b) Growth of the ASE band is observed to be superlinear following subtraction of the strong spontaneous PL background with a clear threshold of ~0.2 mW (linear fit slopes below and above threshold on the log−log plot are indicated). Growth of the spontaneous PL band exhibits sublinear power dependence due to the saturation of the population of the lowest quantized states as indicated by absorption saturation results in Figure 1b. (c) Extracted ASE bands (spontaneous PL subtracted) from multiple samples exhibit size tunability over a range of ~1425−1625 nm.

very high NC densities (>20% volume fractions), well above what is required to produce ASE.

However, our experiments with self-assembled PbSe NC films indicate that because of a relatively weak binding of capping molecules to the PbSe NC surfaces, these films rapidly degrade

under the intense laser illumination and do not allow realization of the ASE regime. To improve the stability of PbSe NCs in the solid-state form, we have developed a new procedure for incorporating NCs into transparent titania sol–gel matrixes. Because the surface chemistry of the PbSe NCs is different from the behavior of CdSe NCs, the previously reported routes to CdSe–titania nanocomposites[5,6] that involved ligand surface exchange are not directly applicable to the PbSe NCs. Here, we use an amphiphilic polymer to complex the PbSe NCs that bypasses the surface exchange and renders the NCs alcohol-soluble.[21] Though some of the hydrophilic COOH moieties on the polymer can bind to the NC surface, others will be found along the periphery of the NC-polymer complex, providing the reactive sites that allow the NCs to be directly tethered to the titania network (Figure 2a). As illustrated in Figure 2b, the absorption spectrum of PbSe NCs after incorporation into the titania matrix maintains the same sharp features as the original solution, indicating a high monodispersity of NCs in the solid-state form. Further, via combined optical and profilometry measurements, we infer very high NC filling factors (~15%), which are well above the critical density required for the development of ASE.

For ASE studies, we fabricate high optical quality sol–gel/NC films (~1–2 μm thickness) on quartz slides by spin-coating (planar waveguide configuration). The films are pumped with a laser beam focused into a narrow stripe of approximately 1 cm length. To facilitate the development of ASE we use uncompressed, 200 ps pulses from an amplified Ti-sapphire laser, which allow us to extend the duration of the optical gain beyond its "natural" Auger-recombination-limited lifetime. As the pump level is gradually increased, we first observe a spectrally uniform growth of the spontaneous PL band (maximum at 1490 nm) with an initial linear increase followed by saturation due to the transition to the Auger recombination regime. At higher pump levels, a new band rapidly grows on the red side of the spontaneous PL (1555 nm). Following the subtraction of the background resulting from the "saturated" spontaneous emission, this new band shows a well-defined threshold (~0.2 mW) and a clear superlinear growth; both of these observations are signatures of the ASE regime. The spectral width of the extracted ASE band (Figure 3) is significantly narrower (by a factor of 3.2) than the width of the spontaneous emission band and does not show significant changes with increasing pump level (similar behavior is observed in CdSe NCs[22]), which is likely due to NC heterogeneity in the sample. Control experiments performed on both dilute solutions and low-filling factor (<3–5%) films do not show the 1555 nm band, indicating that it is not due to "intra-NC" nonlinear effects, such as multiexciton recombination.[23] Further, the ASE mechanism is confirmed by the fact that in pump dependent measurements on high-filling factor samples, the 1555 nm emission only develops at sufficiently long stripe lengths, which is consistent with a strong (exponential) dependence of the emission intensity on the amplification length expected for the ASE regime. We have observed ASE for multiple sol–gel/NC films at both liquid nitrogen and room temperatures; the room-temperature threshold is a factor of 2 higher than at cryogenic temperatures because of a decrease in film optical quality due to thermal effects.

"Active" solid-state PbSe NC nanocomposites demonstrated in this Letter have significant technological potential. The gain spectrum of sol–gel glasses activated with 4.8 nm diameter NCs extends from 1450 to 1550 nm, which covers the 1.5 μm telecommunications window. Compared to Er-doped fibers that are typically used for light amplification in this spectral range (20–30 nm bandwidth and 0.01 cm^{-1} gain), these new NC-activated glasses, for just a single size, offer significantly greater bandwidth and higher gain magnitude (100–150 nm and ~100 cm^{-1}). The large refractive index (1.8–1.9) and high optical quality of sol–gel films allow one to directly use them as planar optical waveguides. The NC nanocomposites can also be easily processed into structures of other geometries (e.g., uniform cylindrical or structured photonic fibers) or combined with feedback elements (e.g., distributed feedback gratings) to enter the lasing regime.

Acknowledgment. This work was supported by the Chemical Sciences, Biosciences, and Geosciences Division of the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy and Los Alamos LDRD funds. We thank Andrew P. Bartko for assistance with atomic force microscopy.

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